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# Some Fundamental Aspects of Solidification in a Supercooled Melt

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# SOME FUNDAMENTAL ASPECTS OF SOLIDIFICATION IN A SUPERCOOLED MELT

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## 1. INTRODUCTION

Dendritic growth in a pure melt can only occur in the presence of a negative temperature gradient in the bulk liquid ahead of the dendrite tips, in other words, in a supercooled bath since even a small positive temperature gradient in the liquid can suppress dendrite formation<sup>(1)</sup>. In an alloy melt, however, dendritic growth occurs quite readily with both positive and negative temperature gradients in the bulk liquid. This is because of the "constitutional supercooling" developing in the bulk liquid due to the compositional changes accompanying the growth process<sup>(2-4)</sup>. The main purpose of this paper is to discuss dendritic growth as it occurs in an "undercooled" or "supercooled" melt.

## 2. DENDRITE TIP UNDERCOOLING VERSUS BATH SUPERCOOLING

When solidification occurs in a positive temperature gradient, in an alloy melt, the temperature of the advancing solid-liquid interface (be it planar, cellular or dendritic) is always depressed below the equilibrium liquidus temperature,  $T_L$ , for the initial alloy

composition,  $C_0$ , by an amount  $\Delta T$  which includes the contributions due to the compositional changes occurring in the liquid, curvature, and kinetic effects<sup>(4)</sup>. During cellular or dendritic growth, this depression in the interface temperature is usually referred to as the "tip undercooling"<sup>(5,6)</sup>. It is important to recognize that steady-state cellular or dendritic growth will always occur with such an "undercooling", even if the first solid were to nucleate at exactly the liquidus temperature  $T_L$ . Likewise, if nucleation occurs after the molten alloy bath has been cooled to some temperature,  $T_\infty$ , well below the liquidus, the temperature at the advancing interface will quickly rise to some value above  $T_\infty$ . The temperature gradient,  $G_L$ , in the bulk liquid ahead of the advancing tips will, therefore, become negative as shown schematically in Figure 1. The temperature gradient within the interdendritic regions,  $G_i$ , may, however, be positive or negative<sup>(7)</sup>. Here it will be assumed that  $G_i > 0$ . Note that the dendrite tip temperature,  $T_t$ , is still depressed below  $T_L$  by an amount  $\Delta T$  given by:

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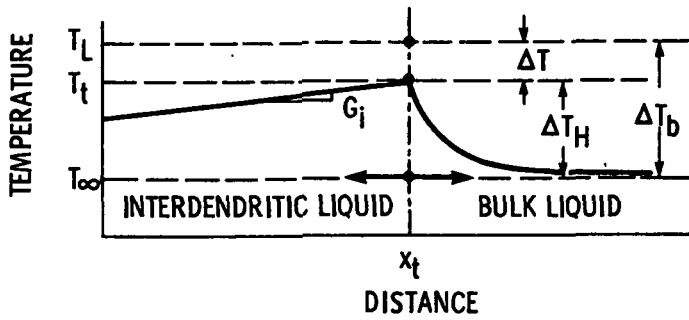


Figure 1: Temperature distribution during dendritic growth in a supercooled alloy melt.

$$\frac{\Delta T}{\Delta T_0} = \left\{ \frac{ak}{k-1} + \frac{Rk}{D_L} \left( 1 - \frac{ak}{k-1} \right) \lambda_c r_t + \frac{2\lambda_c k}{r_t} \right\} \quad (1)$$

Here  $\lambda_c$  is a dimensionless quantity related to the "effective" diffusion distance  $\delta$  in the bulk liquid ahead of the dendrite tips;  $\delta = \lambda_c r_t$ ,  $r_t$  being the tip radius. The other symbols in equation have been defined in a companion paper in this volume<sup>(4)</sup>. Equation (1) above assumes that the kinetic undercooling,  $\Delta T_k \approx 0$  and that the Peclet number  $p \ll 1/2\lambda_c(1-k)$ ;  $p = Rr_t/2D_L$ . The bulk liquid far away from the dendrite tip is depressed, below  $T_L$ , by an amount  $\Delta T_b = (T_L - T_\infty)$ . In what follows,  $\Delta T_b$  will be referred to as the bath "supercooling". The term "undercooling" will be used exclusively to describe the depression in the tip temperature. Finally, it must be emphasized here that the dimensionless parameter  $a = D_L G_i / m_L R C_0$  includes only the interdendritic temperature gradient  $G_i$ <sup>(2,3)</sup>.

### 3. DENDRITE STRUCTURE IN A SUPERCOOLED MELT

Recent direct, in-situ, observations on dendrites growing in transparent materials such as pure succinonitrile (SCN), pivalic acid and in dilute alloys of SCN containing argon or acetone<sup>(8,9)</sup> indicate that the dendrite tip is a paraboloid of revolution with side-branches developing at a short distance behind the tip. However, this characteristic branched structure begins to degenerate to a simpler cylindrical form at moderately large bath supercoolings, whereas at very large bath supercoolings

(typically about 170 K in most ferrous alloys) there is an abrupt transition from a cylindrical to a spherical microstructure<sup>(10)</sup>.

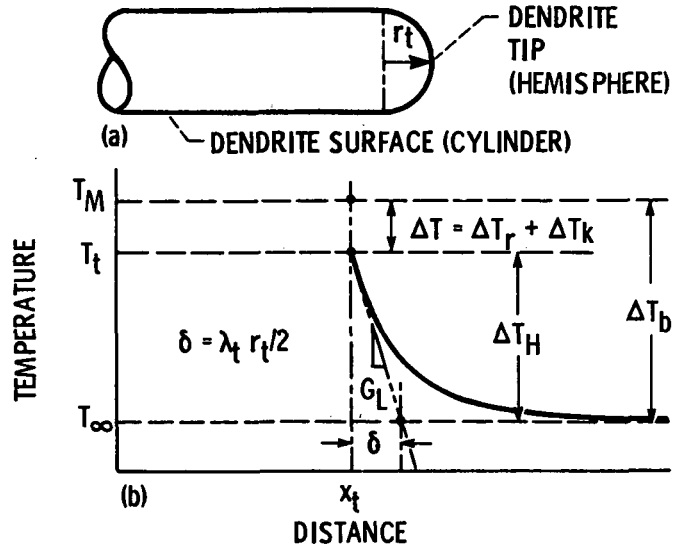


Figure 2: Dendritic growth in a supercooled pure melt.

The so-called "Fisher dendrite" which is assumed to have a hemispherical tip and a cylindrical body<sup>(11)</sup>, Figure 2a, has a morphology remarkably similar to the microstructure observed in moderately supercooled melts. The solution to this dendrite shape, as it applies to a supercooled pure melt will be discussed next followed by a discussion of solidification in a supercooled alloy.

### 4. DENDRITIC GROWTH IN A SUPERCOOLED PURE MELT

Figure 2b illustrates schematically the temperature distribution in the bulk liquid. Let  $G_L$  be the temperature gradient in the liquid at exactly the dendrite tip.  $G_L = -(T_t - T_\infty)/\delta$  where  $\delta$  is now the "effective" thermal diffusion distance. This is simply the distance into the liquid at which the temperature would drop to  $T_\infty$  if the gradient in the liquid had a constant value  $G_L$ . The tip temperature  $T_t$  is depressed below the equilibrium melting point  $T_M$  by an amount  $\Delta T = (T_M - T_t) = \Delta T_r + \Delta T_k$  where  $\Delta T_r$  and  $\Delta T_k$  are respectively the depression in tip temperature (or "undercooling")



$$T_t = T_\infty + \frac{L}{C_p} \left( \frac{\lambda_t R t}{2\alpha_L} \right) \quad (2)$$

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For equilibrium, the tip temperature must also be given by:

$$\tau_t = \tau_M - \frac{L}{C_p} \left( \frac{2d_o}{r_t} \right) \quad (3)$$

where  $d_0$  is a characteristic length called the capillary length<sup>(8)</sup>. Combining equations (2) and (3) above yields

$$\Delta \theta = \frac{T_M - T_\infty}{L/C_p} = \lambda_t \left( \frac{Rr_t}{2\alpha_L} \right) + \frac{2d_0}{r_t} \quad (4)$$

Figure 3 plots schematically the tip temperatures given by equations (2) and (3) respectively as a function of the tip radius. Clearly, steady-state solidification can only occur when the tip radius has the value  $r_1$  or  $r_2$  given by the intersection of these two plots. These radii are given by the following quadratic expression for  $r_t$ :

$$r_t^2(R/R_m) - 4R_c r_t + 4r_c^2 = 0 \quad (5)$$

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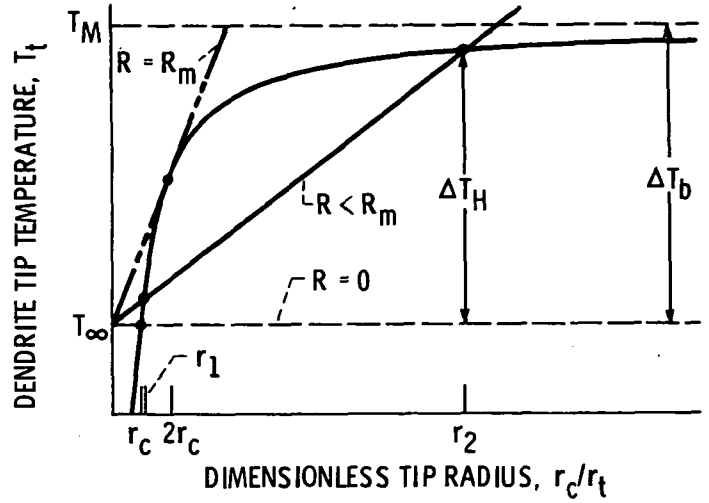


Figure 3: Schematic plot of tip temperature versus tip radius given by equations (2) and (3).

possible growth rate, for a given  $\Delta T_b$ . Previous analyses have simply assumed that the dendrite grows at this maximum growth rate<sup>(8,12)</sup>, for which the tip radius  $r_t = 2r_c$  and the tip temperature  $T_t = (T_M + T_\infty)/2$ . Thus, for  $R = R_m$ ,  $\Delta T = \Delta T_H$ ; so that exactly one-half of the total bath supercooling  $\Delta T_b$  is required to dissipate the heat of fusion.

Figure 3 clearly illustrates that the "maximum velocity" hypothesis has no firm basis and that steady-state growth can occur at a growth rate  $R < R_m$ . However, it is not immediately obvious what dictates the choice between the two possible radii  $r_1$  and  $r_2$ . Rewriting equation (5) as follows:

$$\sigma = \frac{2\alpha_L d_0}{Rr_t^2} = \frac{\lambda_t}{2} \left( \frac{r_t}{r_c} - 1 \right)^{-1} \quad (6)$$

Here  $\sigma$  is a dimensionless parameter characteristic of the dendritic growth process<sup>(14)</sup>. For  $R \ll R_m$ , this parameter, for the larger radius  $r_2$  given by equation (5) is approximately equal to

$$\sigma = \frac{\lambda_t}{8} \left( \frac{R/R_m}{1 - R/4R_m} \right) \quad (7)$$

and, for the smaller radius  $r_1$ ,  $\sigma \approx -\lambda_t/2$ . For  $R = R_m$ ,  $\sigma$  is exactly  $\lambda_t/2$ .

It is important to note here that the parameter  $\sigma$  obtained here is exactly the "tip stability" parameter obtained by Langer and Muller-Krumbhaar<sup>(14)</sup>.  $\sigma$  follows naturally from the analysis of steady-state solidification as discussed here. It may be calculated simply by knowing either the dendrite tip growth rate,  $R$ , or the tip radius,  $r_t$ , provided  $\lambda_t$  is known. It has usually been assumed that  $\lambda_t \approx 1$  but this need not be true<sup>(3,4)</sup>. Thus, for pure SCN<sup>(15)</sup>, the measured tip radius at  $\Delta\theta = 0.001$  is about 30  $\mu\text{m}$  and the observed growth rate  $R = 10 \mu\text{m/sec}$ . At this supercooling,  $r_c = 0.54 \mu\text{m}$  and  $R_m = 1037/\lambda_t$  m/sec, giving  $\lambda_t \approx 7.466$ . Thus, the "effective" thermal diffusion distance is almost four times the tip radius at this supercooling.

Langer and Muller-Krumbhaar observed that for  $\sigma$  greater than a critical value,  $\sigma^*$ , side-branching along the dendrite surface greatly decreases. Thus, it may be argued that "cylindrical" (and also, "spherical") growth morphology observed in moderately supercooled melts correspond to dendritic growth with large values of  $\sigma$ . This simply implies that dendritic growth will occur at smaller values of the ratio  $r_t/r_c$  with increasing bath supercoolings.

## 5. DENDRITIC GROWTH IN A SUPERCOOLED ALLOY MELT

In an alloy melt, steady-state solidification will occur with a tip radius which satisfies both equations (1) and (2) simultaneously:

$$\frac{\Delta T_b - a m_L C_0}{\Delta T_0} = 2\lambda_c \beta k (1 + \epsilon) \frac{R r_t}{2D_L} + \frac{2\lambda_c k}{r_t} \quad (8)$$

$$\text{where } \epsilon = \frac{D_L \lambda_t / 2}{\lambda_c \beta k \alpha_L \Delta T_0 (C_p/L)} \quad (9)$$

and  $\beta = 1 - ak/(k-1)$ . In metal alloys,  $D_L/\alpha_L$  is typically about  $10^{-3}$ , so that,  $\epsilon$  is negligibly small, especially at large growth rates for which  $\beta \approx 1$  since  $a \approx 0$ . Thus equations (4) and (8) are remarkably similar if  $a \approx 0$  and  $\epsilon \approx 0$  with  $\lambda_t$ ,  $\alpha_L$  and  $d_0$  being replaced by their chemical counterparts  $\lambda_c$ ,  $D_L$  and  $\lambda_c$ . For a pure metal the partition ratio  $k = 1$ . Note that  $a \approx 0$  both for very large growth rates and also if the interdendritic concentration gradient,  $G_i/m_L$ , is negligibly small<sup>(3)</sup>. Thus it may be argued that  $a \approx 0$  when spherical particles grow in a supercooled alloy melt, since within a spherical particle there are no "interdendritic channels" through which solute diffusion takes place. Equation (8) may, therefore, also be used to describe solidification in a highly supercooled melt.

Rewriting equation (8) yields a dimensionless parameter  $\sigma_c = 2\lambda_c D_L / R r_t^2$ , given by:

$$\sigma_c = \lambda_c (1 + \epsilon) \left( \frac{r^*}{r_t} - 1 \right) \quad (10)$$

$$\text{where } r^* = \frac{D_L / Rk}{\lambda_c (1 + \epsilon) \Delta T_0 / \Delta T_b}$$

Note that  $\sigma_c$  is the chemical counterpart of the "tip stability" parameter  $\sigma$  defined earlier<sup>(16)</sup>. For  $r_t > r^*$ ,  $\sigma_c$  will become negative.  $r^*$  thus represents the maximum particle size or the tip radius for a given growth rate and bath supercooling. The smallest particle size is, of course, the critical nucleation radius,  $r_c$ , which may be obtained from equation (8) directly by setting  $R = 0$ , with  $\beta = 1$ ,  $a = 0$ . Thus,  $r_c = 2\lambda_c k \Delta T_0 / \Delta T_b$ , and,

$$\frac{r^*}{r_c} = \frac{D_L/2\lambda_c k^2}{R} \left( \frac{\Delta T_b}{\Delta T_0} \right)^2 \frac{1}{\lambda_c(1+\xi)} \quad (12)$$

Recall that  $R_a = D_L/\lambda_c k^2$  is the growth velocity above which a planar interface will remain stable according to the "absolute stability" criterion<sup>(4,17)</sup>. At these large growth rates  $\sigma_c$  becomes negligibly small since  $\lambda_c$  also tends to zero<sup>(3,4)</sup> at large values of  $R$ . This may be interpreted as implying "solute trapping" or "partitionless" solidification for which  $k$  tends to unity. More importantly, equation (10) clearly indicates that the "tip stability" parameter  $\sigma_c$  is the underlying fundamental quantity governing these transitions. Finally, it may be noted that the stability parameters  $\sigma$  and  $\sigma_c$  are both related to the respective dimensionless length scales  $\lambda_t$  and  $\lambda_c$ .

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| 16. Abstract<br><br>A model for dendritic growth in both supercooled pure and alloy melts has been presented. In a pure melt, dendrite morphology is determined by the value of the dimensionless parameter $\sigma = 2\alpha_L d_0 / Rr_t^2$ , whereas, in an alloy melt it is determined by the parameter $\sigma_c = 2k_c D_L / Rr_t^2$ . The application of the above analysis to cylindrical and spherical growth morphologies obtained in highly supercooled melts has been discussed. An upper and lower bound for the particle or tip radius in this case has been obtained in terms of the growth rate and the initial bath supercooling. |  |  |  |   |  |
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